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Magnetocaloric effect in amorphous ribbon based on Finemet

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Abstract : Amorphous ribbons of $Fe_{73.5}Cu_1Nb_3Si_{17.5}B_5$ alloy have been prepared by single roller melt spinning Curie temperature has been measured 344, 345 and 347°C by temperature dependence magnetization, temperature dependence ac permeability and Arrott plot, respectively The onset crystallization temperature is obtained 530°C and above crystallization gradually increase, is related to onset crystallization of α-Fe(Si) ferromagnetic phase in the remaining amorphous matrix Increase of saturation magnetization, M_s can be attributed to the reversible structural relaxation and decreasing correspond to the optimum nanocrystallized state with high volume fraction of α-Fe(Si) nanograins. The giant magnetocaloric effect (GMCE) has been found in amorphous state of the sample. Temperature dependence maximum magnetic entropy of the sample has been obtained as 3.04 J/Kg K around the Curie temperature at moderately low magnetic field change of 1 34 T

Keywords : Finemet, Amorphous materials, Magnetocaloric effect, Nanocrystalline alloy

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1. Introduction

The Magnetocaloric effect (MCE), or adiabatic temperature change (ΔT_{ad}), is defined as the heating or cooling of a magnetic material due to the application of a magnetic field. Upon the application of an external magnetic field, the magnetic spins of magnetic dipoles in a materials attempt to align with the field, thereby reducing the magnetic entropy

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(ΔS_m) and heat capacity of the spin system If this process is performed adiabatically, the temperature of the materials will rise Conversely, when the external magnetic field is removed adiabatically, the magnetic dipoles of the materials disorder and the temperature of the materials will be reduced This temperature change ΔT, referred to as the magnetocaloric effect forms the basis for achieving millidegree Kelvin temperature in single step adiabatic demagnetization coolers The refrigeration community has significant activity occurred to employ the MCE in order to construct a magnetic refrigerator operating at either cryogenic temperature [1, 2] or near room temperature [3, 4]

Most magnetic materials exhibit a large MCE only at low temperature, which is not suitable for domestic usage Recently, there has been interest to develop a new magnetic refrigeration technology as an energy efficient [5] and environmentally safe alternative to eliminate ozone depleting chemicals (CFCs), green house gases (HCFCs and HFCs) and hazardous chemicals (NH_3) *etc* present in high temperature gas cycle system of existing vapor compression refrigeration and as well as operates to near and higher room temperature region

The ΔT_{ad} and ΔS_m are correlated with the magnetization (M), the magnetic field strength (H), the heat capacity at constant pressure (C), and the absolute temperature by one of the fundamental Maxwell's relations [6]

$$\Delta S_m(T\ \Delta H) = \int_{H_1}^{H_2} \left(\frac{\partial M(T,H)}{\partial T} \right)_H dH \tag{1}$$

and

$$\Delta T_{ad}(T, \Delta H) = -\int_{H_1}^{H_2} \left(\frac{T}{C(T,H)} \right)_H \left(\frac{\partial M(T\ H)}{\partial T} \right)_H dH \tag{2}$$

where H_2 is the final applied magnetic field

If one measures the magnetization as a function of field at various temperatures, then the integral in eq (1), and ΔS_m could be the area enclosed between any two isotherms divided by the temperature difference between the isotherm *i e*,

$$\Delta S_m = \sum \frac{M_i - M_{i+1}}{T - T_{i+1}} \Delta H_i \tag{3}$$

where M_i and M_{i+1} are the experimental values of magnetization at T_i and T_{i+1} respectively, under an applied magnetic field of H_i [7]

Franco *et al* [8] reported that the refrigerant capacity (RC) of $Fe_{68.5}Mo_5B_9Cu_1Nb_3$ amorphous alloy is 63 JKg^{-1} for an optimal reversible cycle with cold and hot ends at

55°C and 247°C, respectively for a maximum applied field H = 15 kOe and the Mo-Finemet alloy is more than 20 times cheaper from $Gd_5Ge_{1.9}Si_2Fe_{0.1}$, the applied field employed is smaller and the temperature span of the optimal cycle is increased.

Franco *et al* [9] noted that the influence of Co addition in FeCoSiAlGaPCB bulk amorphous alloy, magnetic entropy has been changed. This composition modification displaces the temperature of the peak entropy change closer to room temperature, but reduces the refrigerant capacity of the material.

The effect of Co addition on the magnetocaloric effect of amorphous alloys with nanoperm type composition has been reported by Franco *et al* [10]. They showed that Co addition produces an increase in the maximum magnetic entropy change and maximum refrigerant capacity (RT) value obtained 82 J Kg^{-1} for a maximum applied field H = 15 kOe. This value is ~ 30% larger than that of a Mo-containing Finemet-type alloy measured under the same condition [8]

Chau *et al* [11] reported that the crystallization volume fraction as well as the particle size of α-Fe(Si) crystallites decreased with increasing Cr amount substituted for Fe in amorphous ribbon of $Fe_{73.5-x}Cr_xSi_{13.5}B_9Nb_3Cu_1$ (x = 1–5). The giant magnetocaloric effect (GMCE) obtained in the range of 9 8–5.1 J/kgK for (x = 1–5) in the amorphous state of the samples.

The prototype materials for the room temperature range is the lanthanide metal Gd which orders ferromagnetically at 21°C [12]. Recently a series of $Gd_5(Si_xGe_{1-x})_4$ alloys, where $0 \le x \le 0.5$, which reported [13, 14] to display a ΔS_m at least two times larger than that of Gd near room temperature and between 2 and 10 times larger than the best magnetocaloric materials in the low and intermediate temperature regions.

In the present work, a $Fe_{73.5}Cu_1Nb_3Si_{17.5}B_5$ amorphous alloy was selected based on the composition of the Finemet alloy and the aim is to study the magnetocaloric effect.

2. Experimental

Amorphous ribbons (10 mm width and 20 μm thickness) of nominal composition $Fe_{73.5}Cu_1Nb_3Si_{17.5}B_5$ based on Finemet have been prepared by melt-spinning method in single roller equipment at the Laboratory of Amorphous Materials in Hanoi University of Technology. The purity of the material is Fe (99.98%), Cu (99+ %), Nb (99.8%), B (99.5%) and Si (99.9%) obtained from Johnson Mathey (Alfa Aesar Inc.). The amorphosity of the ribbons has been examined by XRD experiment carried out in a Philips X-pert Pro X-ray diffractometer with CuK_α radiation. Isotherm magnetization curves were measured by a Vibrating Sample Magnetometer (DMS 880 VSM, USA digital measurement system).

3. Results and discussion

XRD pattern of as cast ribbon sample has been presented in Figure 1. The pattern exhibits only one broad peak around $2\theta = 45^0$, showing that the as cast sample is in the amorphous state. Temperature dependence of initial permeability (μ') of the as cast amorphous

ribbon has been measured by using a laboratory built furnace and Wayne Kerr 3255B impedance analyzer with continuous heating rate of ≈ 5°C/min with very low applied ac field of ≈ 10^{-3} Oe and shown in Figure 2. It is observed from the Figure 2 that permeability passes through a maximum just before a sharp fall to near zero with the manifestation of

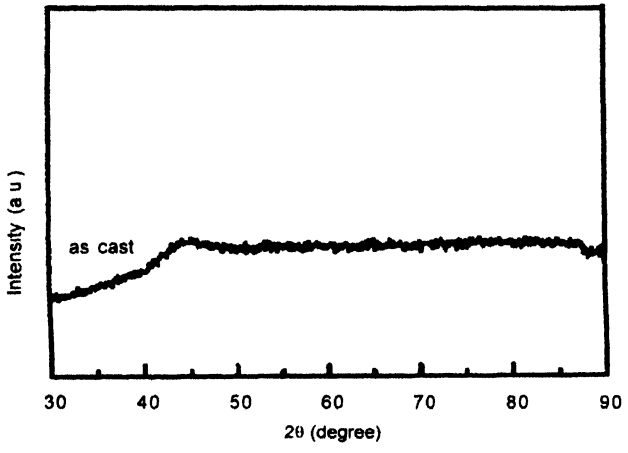

Figure 1. X-ray diffraction pattern of as cast sample of $Fe_{73.5}Cu_1Nb_3Si_{17.5}B_5$

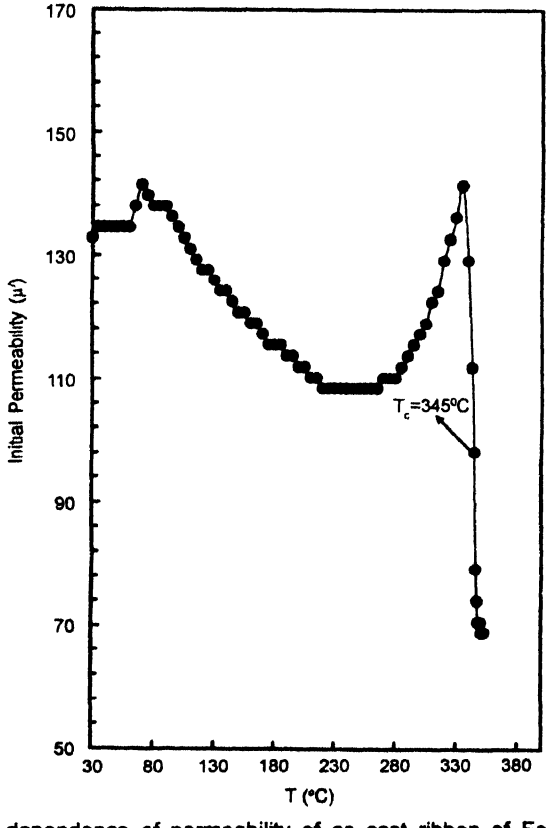

Figure 2. Temperature dependence of permeability of as cast ribbon of $Fe_{73.5}Cu_1Nb_3Si_{17.5}B_5$.

Hopkinson effect characterizing the ferro-paramagnetic transition of the amorphous phase The accurate determination of T_c of the amorphous materials is really difficult due to irreversible components of the structural relaxation like long-range internal stress, topological and chemical short-range order This structural relaxation without destroying the amorphous state may influence T_c Therefore during the measurement of T_c the heating rate has been adjusted in such a way that no substantial relaxation takes place The Curie temperature of the amorphous state of sample is 345°C, as that temperature where the $\delta\mu/\delta T$ attains its maximum value and initial permeability sharply falls from this point

A material is ferromagnetic if it possesses regions of finite magnetization where the external magnetic field intensity $H = 0$ The temperature at which ferromagnetism occurs is called the Curie temperature, T_c, and depends on the strength of exchange interaction which arises from the overlapping of the electronic wave functions of the interacting magnetic atoms

Temperature dependence of low field dc magnetization measured with an applied field of 20 Oe at a heating rate of 20^0C min^{-1} by the VSM is shown in Figure 3 It is observed

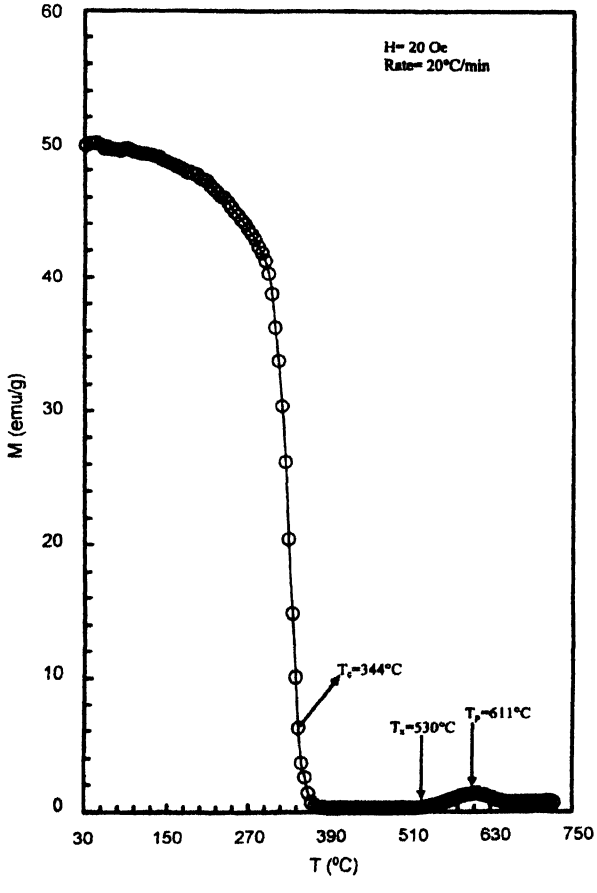

Figure 3. Temperature dependence of magnetization curve of as cast ribbon of $Fe_{73.5}Cu_1Nb_3Si_{17.5}B_5$

that magnetization is fairly constant until the appearance of "Kink point" beyond which magnetization sharply falls to zero Demagnetization fields limits the magnetization to a value of $H = H_a/D$ (where H_a is the applied magnetic field and D is the shape-dependent demagnetization factor), producing a magnetization that is temperature independent below the kink point The characteristics feature of the curve is that magnetization (M) decreases with temperature and passes through ferromagnetic-paramagnetic transition at Curie temperature T_c = 344°C by drawing the linear intercept to X-axis It is more appropriate from the fundamental point of view to find out the T_c from the appearance of spontaneous magnetization as the temperature is decreased (cooling) than the vanishing of spontaneous magnetization as the temperature is increased (warming) because of many complexities of the co-operative phenomena, in particular domain wall motion In general, determination of T_c is not that straight forward as it seems to be from the first principle and the unique value of T_c can be determined without ambiguity only when the material under study is perfectly homogeneous single phase, defect free and of high purity It is observed from the Figure 3 that temperature above T_c^{am} to 530°C, magnetization value is nearly zero since sample are paramagnetic in this temperature range At 530°C and above the crystallization behavior of the amorphous sample has been established as the temperatures gradually increase further This increase of magnetization of the amorphous sample in paramagnetic state is related to the onset of crystallization of α-Fe(Si) ferromagnetic phase in the remaining amorphous matrix From Figure 3, it is also seen that the onset of crystallization temperature (T_x) of the sample is 530°C and the peak temperature (T_p) of α-Fe(Si) is 611°C The characteristics of the M(T) curve follows the similar trend reported by Chau *et al* [7, 11] and Franco *et al* [8] for the Finemet-type amorphous alloy

Figure 4 shows magnetization curves as a function of internal magnetic field up to 13 4 kOe for the sample measured at various temperatures around the Curie temperature T_c The magnetocaloric effect around the T_c is expected to be large [15] So we measured a series of isotherm M(H) at different temperature around the Curie temperature Magnetization rises sharply at extremely low field and then gradually bends over but still rising up to the magnetic field of 12 kOe and saturate at the maximum field 13 4 kOe

Sometimes an operational procedure needs to be adopted for the determination of T_c A standard procedure for determination T_c in ferromagnetic materials is based on symmetry principle Arrott [16], Belov [17], and Kouvel [18] have pioneered the use of classical form of expression for magnetization and field near a ferromagnetic phase transition and showed that internal field, H_i, should be an odd power of magnetization M, and is given by

$$H_i = A(T - T_c)M + BTM^3 + CTM^5 + \quad (4)$$

where A, B, C are constants

Since $M << M_s$, the saturation magnetization around T_c, the terms involving M_5 and higher can be neglected, so the equation can be written as

$$H_i = A(T - T_c)M + BTM^3 \quad (5)$$

$$\text{At } T = T_c; \quad H_i / M = BTM^2$$

Therefore, a value T_c may be determined from magnetic isotherms by ploting at fixed temperatures, M^2 *vs* H_i/M. According to eq. (5) these plots should yield straight lines for

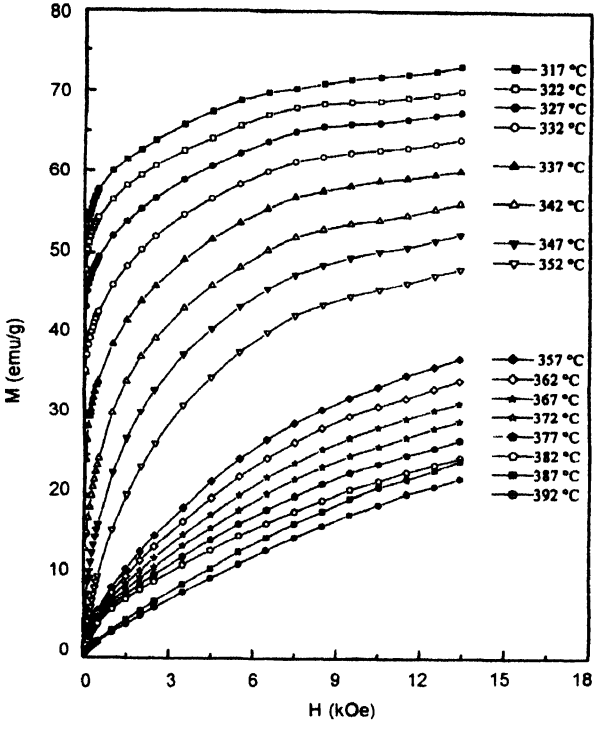

Figure 4. Field dependence magnetization curves of the sample at different temperature

each value of T and T_c corresponds to that straight line which passes through the origin for a low enough field, H_i. These plots are called Arrott-Belov-Kouvel (ABK) plots and

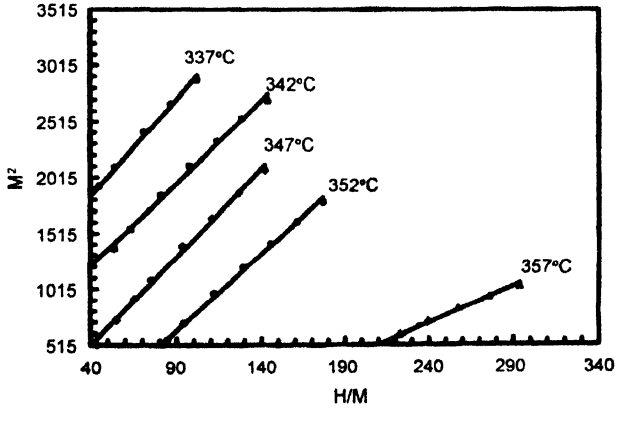

Figure 5. Arrott plots from isotherms of Figure 4 at low magnetic field.

sometimes shortly called Arrott plots Arrott plots demonstrated in Figure 5 are calculated from the magnetic isotherms depicted in Figure 4 Arrott plots from the magnetization data (Figure 5) show that the Curie temperature is close to 347°C as for the line passed through the origin

Figure 6 shows the magnetic entropy of the sample calculated from the field dependence magnetization curves at different temperature around T_c of respective amorphous phase by using the eq (3) It is observed from Figure 6 that magnetic entropy gradually increases and maximum value obtained 3 04 J/Kg K at temperature 352°C and then it drops abruptly The characteristic of the maximum magnetic entropy curve follows the similar trend, reported by Chau *et al* [7, 11] for Finemet-type amorphous alloy

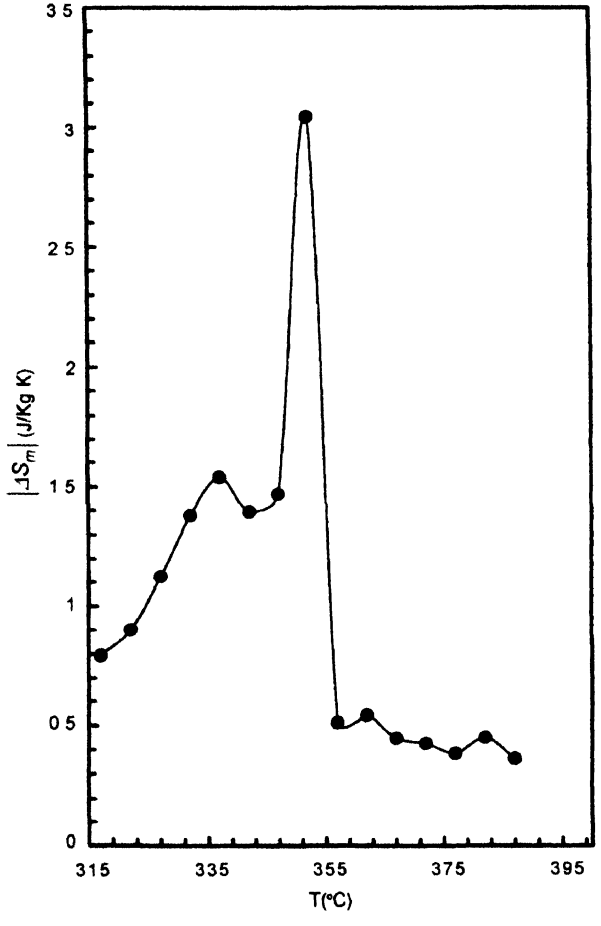

Figure 6. Temperature dependence of magnetic entropy, $|\Delta S_m|$ of amorphous ribbon of $Fe_{73.5}Cu_1Nb_3Si_{17.5}B_5$

4. Conclusion

The magnetic materials based on Finemet have the high saturation magnetization, magnetization sharply changes at ferromagnetic- paramagnetic phase transition of

amorphous state, high working temperature and low heat capacity. These characteristics of magnetic materials are well adapted with the requirements of magnetocaloric effect. The value of maximum magnetic entropy $|\Delta S_m|$ of the sample has been obtained at moderately low magnetic field change of 1.34 T and the studied sample could be used as magnetic refrigerant materials working at high temperature regions

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